**PATENT APPLICATION**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re application of

Docket No: Q87310

Toyoaki ISHIWATA , et al.

Appln. No.: 10/530,414

Group Art Unit: not yet assigned

Confirmation No.: Not yet assigned.

Examiner: not yet assigned

Filed: April 07, 2005

For: POLYIMIDE FILM AND PROCESS FOR ITS PRODUCTION

**SUBMISSION OF ENGLISH LANGUAGE TRANSLATION OF ARTICLE 34 AMENDMENT AND COMMENTS THEREON**

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450
Sir:

Submitted herewith please find an English language translation of the Article 34 Amendment for the above-identified application. Applicants note that in item (5) in the description of the amendment (Content of the Amendment), in which "at least 3 GPa" should be "greater than 3 GPa" (this can be seen from page 28, line 32 in the national stage application filed on April 7, 2005).

Respectfully submitted,

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WASHINGTON OFFICE
23373
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Date: July 7, 2005

AMENDMENT

(pursuant to Article 11 of the Japanese Patent Law)

To: Commissioner of the Japanese Patent Office

1. International Application Classification: PCT/JP03/04085

2. Applicant

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4. Object of the Amendment

(1) Specification

(2) Claims

5. Content of the Amendment

(1) The text "3 GPa or greater" on page 5, line 4, page 7, line 17 and page 11, line 14 of the specification is corrected to "greater than 6 GPa".

(2) The text "at least 3 GPa and more preferably at least 6 GPa" on page 10, line 21 of the specification is corrected to "greater than 6 GPa".

(3) The text "If the Young's modulus is less than 3 GPa,

the rigidity will be insufficient particularly with smaller thicknesses, and the process transportability will often be inferior. The elastic modulus of the obtained polyimide film is preferably at least 3 GPa and more preferably at least 6 GPa in two directions." on page 11, line 16 of the specification is corrected to "If the Young's modulus 6 GPa or less, the rigidity will be insufficient particularly with smaller thicknesses, and the process transportability will often be inferior."

(4) The text "... it has two perpendicular directions in which the Young's modulus is greater than 3 GPa in the plane of the film. Preferably, the plane of the film has two perpendicular directions in which the Young's modulus is greater than 6 GPa." on page 12, line 18 of the specification is corrected to "... it has two perpendicular directions in which the Young's modulus is greater than 6 GPa in the plane of the film."

(5) The text "3 GPa and more preferably at least 6 GPa" on page 24, line 24 of the specification is corrected to "6 GPa".

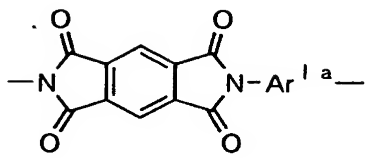
(6) The text "The concentration of the polyamic acid NMP solution was 7 wt%" on page 41, line 1 is corrected to "The concentration of the polyamic acid NMP solution was 7 wt%". [Note: correction of Japanese text].

(7) The text "3 GPa or greater" in claim 1, line 3 from the bottom (second page) is corrected to "greater than 6 GPa".

6. List of Attached Documents

(1) Specification, pages 5, 7, 10, 11, 12, 24, 41 (one copy each)

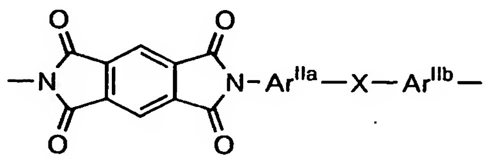
(2) Claims, pages 43, 44 (one copy each)



(I)

[wherein $Ar^{Ia}$ is 1,4-phenylene optionally having a non-reactive substituent], and

a structural unit of the following formula (II) at between 1 mole percent and 70 mole percent:



(II)

(wherein $Ar^{IIa}$ and $Ar^{IIb}$ are each independently a C6-20 aromatic group optionally having an non-reactive substituent, and X in structural unit (II) consists of at least one group selected from among groups of the following formula (II-i):

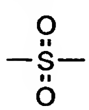
-O- (II-i)

the following formula (II-ii):

$-O-Ar^{IIc}-O-$ (II-ii)

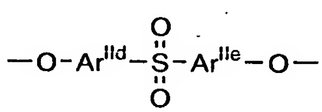
[wherein $Ar^{IIc}$ is a C6-20 aromatic group optionally having a non-reactive substituent],

the following formula (II-iii):



(II-iii)

and the following formula (II-iv):



(II-iv)

[wherein $Ar^{IId}$ and $Ar^{IIe}$ are each independently a C6-20 aromatic group optionally having a non-reactive substituent],

the polyimide film being characterized by having two perpendicular directions in which the in-plane Young's modulus is greater than 6 GPa, and having a moisture absorptivity of

no greater than 3.3 wt% at 72% RH, 25°C.

The present invention is the result of examining techniques for high degree stretching and molecular orientation of aromatic polyimides with rigid structures, and it provides a polyimide film having an in-plane balance of mechanical properties and enhanced moist heat resistance and absorptivity, by copolymerization of structural unit (II) in a specific amount with respect to structural unit (I).

According to the invention, the aforementioned objects and advantages are achieved, secondly, by a film-forming process of a polyimide film characterized by comprising the following steps:

Step 1: A step in which (A) pyromellitic anhydride, (B) an aromatic diamine compound represented by the following formula (III):

$$H_2N-Ar^{Ia}-NH_2 \qquad (III)$$

[wherein $Ar^{Ia}$ is 1,4-phenylene optionally having a non-reactive substituent],

and (C) an aromatic diamine compound represented by the following formula (IV):

$$H_2N-Ar^{IIa}-X-Ar^{IIb}-NH_2 \qquad (IV)$$

(wherein $Ar^{IIa}$ and $Ar^{IIb}$ are each independently a C6-20 aromatic group optionally having an non-reactive substituent, and X consists of at least one group selected from among groups of the following formula (IV-i):

$$-O- \qquad (IV\text{-}i)$$

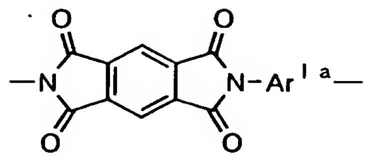
the following formula (IV-ii):

$$-O-Ar^{IIc}-O- \qquad (IV\text{-}ii)$$

[wherein $Ar^{IIc}$ is a C6-20 aromatic group optionally having a non-reactive substituent],

the following formula (IV-iii):

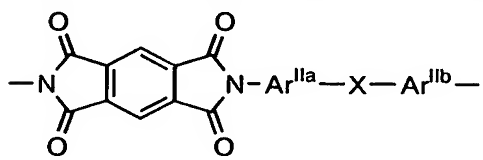
$$-\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}- \qquad (IV\text{-}iii)$$



(I)

[wherein $Ar^{Ia}$ is 1,4-phenylene optionally having a non-reactive substituent], and

a structural unit of the following formula (II) at between 1 mole percent and 70 mole percent:



(II)

(wherein $Ar^{IIa}$ and $Ar^{IIb}$ are each independently a C6-20 aromatic group optionally having an non-reactive substituent, and X in structural unit (II) consists of at least one group selected from among groups of the following formula (II-i):

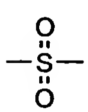
-O- (II-i)

the following formula (II-ii):

$-O-Ar^{IIc}-O-$ (II-ii)

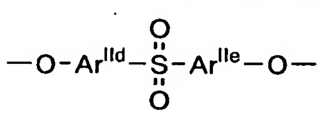
[wherein $Ar^{IIc}$ is a C6-20 aromatic group optionally having a non-reactive substituent],

the following formula (II-iii):



(II-iii)

and the following formula (II-iv):



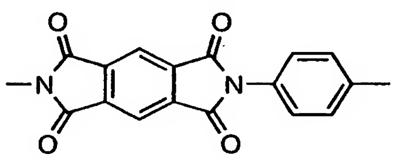
(II-iv)

[wherein $Ar^{IId}$ and $Ar^{IIe}$ are each independently a C6-20 aromatic group optionally having a non-reactive substituent],

the polyimide film being characterized by having two perpendicular directions in which the in-plane Young's modulus is greater than 6 GPa, and having a moisture absorptivity of

no greater than 3.3 wt% at 72% RH, 25° C.

$Ar^{Ia}$ in formula (I) above is 1,4-phenylene optionally having a non-reactive substituent, and examples of non-reactive substituents include C1-6 alkyl groups such as methyl, C1-6 alkoxy groups such as methoxy, and halogens such as chlorine and fluorine. Preferred examples of $Ar^{Ia}$ include 1,4-phenylene, 1,3-phenylene, 2-chloro-1,4-phenylene, 2-methyl-1,4-phenylene, 2,5-dichloro-1,4-phenylene, 2,5-dimethyl-1,4-phenylene, 2-chloro-5-methyl-1,4-phenylene and 2-methoxy-1,4-phenylene. As a more preferred example there may be mentioned 1,4-phenylene. Specifically, a particularly preferred example of structural unit (I) is the following formula (I-a):



(I-a)

Two or more compounds of structural unit (I) may also be used in combination.

$Ar^{IIa}$ and $Ar^{IIb}$ are each independently a C6-20 aromatic group optionally having an non-reactive substituent. As aromatic groups there may be mentioned phenylene, naphthylene and biphenylene. The aromatic groups may also have some or all of the hydrogens substituted with non-reactive substituents. Such non-reactive substituents may include C1-6 alkyl groups such as methyl, C1-6 alkoxy groups such as methoxy, and halogens such as chlorine and fluorine. Preferred examples of $Ar^{IIa}$ and $Ar^{IIb}$ in structural unit (II) include 1,4-phenylene and/or 1,3-phenylene.

X in structural unit (II) consists of at least one group selected from among groups of formulas (II-i), (II-ii), (II-iii) and (II-iv) above.

When X is a group of formula (II-i), a particularly preferred example is a compound wherein $Ar^{IIa}$ and $Ar^{IIb}$ in structural unit (II) comprises a combination of 1,4-phenylene

Formula (II-iv-a) may be mentioned as a particularly preferred example among these.

Preferably, X in structural unit (II) is represented by formula (II-i), with 40-70 mole percent of structural unit (I) and 30-60 mole percent of structural unit (II). This structure will yield a polyimide film with an adequate Young's modulus and excellent moist heat resistance.

The elastic modulus of the obtained polyimide film is greater than 6 GPa in two directions.

Preferably, X in structural unit (II) is at least one group selected from among (II-ii), (II-iii) and (II-iv), with 60-90 mole percent of structural unit (I) and 10-40 mole percent of structural unit (II).

Research for the present invention revealed that the imide group concentration in the polyimide is an important factor for obtaining a polyimide film having an adequate Young's modulus and excellent moist heat resistance. More specifically, the preferred composition for a polyimide film having an adequate Young's modulus and excellent moist heat resistance is a composition wherein the imide group concentration, [imide] is 5.7-6.2 eq/kg. More preferably, it is 5.8-6.1 eq/kg and even more preferably 5.85-6.05 eq/kg. The imide group concentration is the value representing the equivalents of imide groups in 1 kg of the polyimide.

This composition can yield a polyimide film with an adequate Young's modulus and excellent moist heat resistance.

The polyimide film of the invention has excellent practical properties, with a hitherto unprecedented high value for the Young's modulus and a satisfactory balance thereof. That is, it has two perpendicular directions in which the in-plane Young's modulus is greater than 6 GPa. If the Young's modulus is 6 GPa or less, the rigidity will be insufficient particularly with smaller thicknesses, and the process transportability will often be inferior.

The polyimide film of the invention has a moisture absorptivity of no greater than 3.3 wt% at 72% RH, 25°C. It is preferably not 3.3 wt% or greater because high temperature heat treatment may result in decomposition of the polyimide film, or foaming due to rapid expansion of moisture. The moisture absorptivity is more preferably no greater than 3.1 wt% and even more preferably no greater than 2.9 wt%.

The polyimide film of the invention preferably has a tensile strength of at least 150 MPa in one direction. This is more preferably at least 180 MPa and even more preferably at least 200 MPa.

The polyimide film of the invention also preferably has a tensile breaking elongation of at least 3% in one direction. This is more preferably at least 5% and even more preferably at least 10%.

The imide group fraction in the polyimide of the polyimide film of the invention is preferably at least 95%. The imide group fraction is preferably not less than 95% because the hydrolysis resistance of the polyimide film will be reduced.

The imide group fraction is the proportion (mole percent) of imide group nitrogen atoms with respect to the total of the amic acid nitrogen atoms and imide group nitrogen atoms in the polyimide film.

As a result of studying techniques for high degree stretching and molecular orientation of aromatic polyimides with rigid structures, the present inventors discovered that a gel prepared by employing a specific process for chemical treatment of a precursor amic acid, having structural unit (II) copolymerized in a specific amount with structural unit (I), has a high stretching property at low temperatures near room temperature, and that therefore stretching of the gel in an expanded state followed by heat treatment can yield a polyimide film with an excellent Young's modulus, a balance of in-plane mechanical properties and improved moisture

absorptivity.

The imide group fraction in the polyimide of the polyimide film of the invention is preferably at least 95%. The imide group fraction is preferably not less than 95% because the hydrolysis resistance of the polyimide film will be reduced. The imide group fraction is defined in the examples.

The polyimide film of the invention has excellent practical properties, including a hitherto unprecedented high value for the Young's modulus and a satisfactory balance of the Young's modulus in the film plane. That is, it has two perpendicular directions in which the Young's modulus is greater than 6 GPa in the plane of the film.

The polyimide film of the invention preferably has a tensile strength of at least 150 MPa in one direction. The tensile strength is more preferably at least 300 MPa and even more preferably at least 400 MPa in one direction.

The production process for the polyimide film of the invention will now be explained.

The production process of the invention comprises the following steps (1) to (4).

Step 1: A step in which (A) pyromellitic anhydride, (B) an aromatic diamine compound represented by the following formula (III):

$$H_2N-Ar^{Ia}-NH_2 \qquad (III)$$

[wherein $Ar^{Ia}$ is 1,4-phenylene optionally having a non-reactive substituent],

and (C) an aromatic diamine compound represented by the following formula (IV):

$$H_2N-Ar^{IIa}-X-Ar^{IIb}-NH_2 \qquad (IV)$$

(wherein $Ar^{IIa}$ and $Ar^{IIb}$ are each independently a C6-20 aromatic group optionally having an non-reactive substituent, and X consists of at least one group selected from among groups of the following formula (IV-i):

$$-O- \qquad \text{(IV-i)}$$

the following formula (IV-ii):

$$-O-Ar^{IIc}-O- \qquad \text{(IV-ii)}$$

[wherein $Ar^{IIc}$ is a C6-20 aromatic group optionally having a non-reactive substituent],

the following formula (IV-iii):

$$-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}- \qquad \text{(IV-iii)}$$

and the following formula (IV-iv):

$$-O-Ar^{IId}-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-Ar^{IIe}-O- \qquad \text{(IV-iv)}$$

[wherein $Ar^{IId}$ and $Ar^{IIe}$ are each independently a C6-20 aromatic group optionally having a non-reactive substituent],

are reacted in a solvent in proportions simultaneously satisfying the following inequalities (1) and (2):

$$0.95 \leq a/(b+c) \leq 1.05 \qquad (1)$$

$$0.01 \leq c/(b+c) \leq 0.70 \qquad (2)$$

[wherein a is the number of moles of pyromellitic anhydride, b is the number of moles of the aromatic diamine compound represented by formula (III) above, and c is the number of moles of the aromatic diamine compound represented by formula (IV) above]

to obtain a polyamic acid solution;

Step 2: A step of reacting the obtained polyamic acid solution with a dehydrating agent to form a gel film wherein at least a portion of the polyamic acid is converted to polyisoimide;

Step 3: A step of biaxially stretching the obtained gel film;

Step 4: A step of heat treating the obtained biaxially stretched film.

In Step 1, solution polymerization of the polyamic acid is carried out to prepare a polyamic acid solution. Any

or heating by contact with a hot plate, hot roll or the like. Stepwise raising of the temperature is preferred in order to promote removal and drying of the solvent, imidation and/or conversion of isoimides to imides.

The heat treatment may be carried out at a constant length or under tension. The heat treatment temperature is not particularly restricted in terms of the initial temperature, but the maximum temperature for the heat treatment is preferably 250-650° C. It may be carried out while gradually raising and/or lowering the temperature in stages. In any case, the heat treatment can inhibit relaxation of the orientation while obtaining a polyimide film with an imidation rate of over 95%. Heat treatment at below 250° C is not preferred as it will not easily produce an imidation rate of over 95%, or may require a longer time to achieve an imidation rate of over 95%. Heat treatment at above 650° C is also not preferred because it may cause heat degradation of the polyimide. The temperature is preferably 300-600° C and more preferably 350-550° C.

The biaxially oriented polyimide film obtained in the manner described above has its molecular chains strongly oriented in the plane of the film and is therefore a polyimide film having a high Young's modulus with an excellent in-plane balance and exhibiting enhanced strength, since its Young's modulus measured in two orthogonal directions in the plane will be greater than 6 GPa, and a special microstructure is formed by stretching orientation. This high Young's modulus polyimide film is highly rigid and can therefore be suitably used for electronic purposes, and for example, as a support for electrical wiring boards laminated with thin copper films, even if the film has a small thickness of 10 μm or smaller. It may also be used as a support for metal wiring circuit boards, flexible circuit boards, TAB (tape automated bonding) tape and LOC (lead-on-chip) tape. It may also be used as a base film for magnetic recording tape.

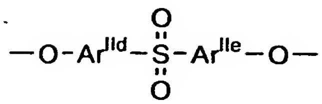
Table 3

| | I (mol%) | II (mol%) | Thickness (μm) | PCT | Measuring direction | Young's modulus (GPa) | Strength (MPa) | Elonga -tion (%) | Moist-ure absorp-tivity (%) | Imide group frac-tion (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| Example 13 | 90 | 10 | 17 | untreated | MD<br>TD | 16<br>15 | 428<br>407 | 12<br>11 | 3.1 | 99 |
| Example 14 | 90 | 10 | 26 | untreated | MD<br>TD | 13<br>13 | 392<br>372 | 8<br>7 | 3.2 | 99 |
| Example 15 | 90 | 10 | 25 | untreated | MD<br>TD | 12<br>11 | 314<br>284 | 5<br>7 | 3.2 | 99 |
| Example 16 | 90 | 10 | 29 | untreated | MD<br>TD | 13<br>11 | 368<br>381 | 10<br>10 | 3.3 | 99 |
| Example 17 | 70 | 30 | 10 | untreated | MD<br>TD | 11<br>10 | 373<br>354 | 21<br>18 | 1.8 | 99 |
| Example 18 | 90 | 10 | 16 | untreated | MD<br>TD | 16<br>16 | 380<br>392 | 9<br>10 | 3.0 | 99 |
| Example 19 | 90 | 10 | 17 | untreated | MD<br>TD | 15<br>14 | 378<br>381 | 11<br>10 | 3.1 | 99 |

Example 20

After placing 20 L of dehydrated NMP with a moisture content of 10 ppm in a reactor equipped with a thermometer, stirrer and starting material charging inlet under a nitrogen atmosphere, 225.29 g of p-phenylenediamine and 417.41 g of 3,4'-DAPE (aromatic diamine compound represented by formula (IV-i-a) above) were added and the mixture was thoroughly dissolved. It was then cooled in an ice bath to adjust the diamine solution temperature to -5° C. Next, 909.08 g of pyromellitic anhydride was added to the cooled diamine solution and reaction was conducted for 1 hour. the temperature of the reaction solution was 0-5° C. The reaction solution was reacted for 4 hours at 10-15° C. Next, 1.23 g of phthalic anhydride was added and reacted therewith for 2 hours for amine end capping, to obtain a polyamic acid NMP solution as a viscous solution. The concentration of the polyamic acid NMP solution was 7 wt%, and the reducing viscosity of the polyamic acid was 9.1.

The obtained 7 wt% polyamic acid NMP solution was cooled to -10° C under a nitrogen atmosphere, and then pyridine was added at a proportion of 4 moles of pyridine to 1 mole of polyamic acid repeating units, mixing was performed with a static mixer, acetic anhydride was added at a proportion of 6



(II-iv)

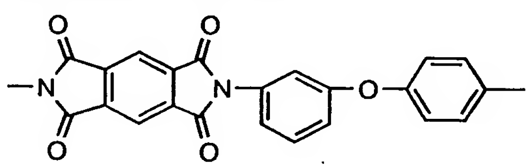
[wherein $Ar^{IId}$ and $Ar^{IIe}$ are each independently a C6-20 aromatic group optionally having a non-reactive substituent], the polyimide film being characterized by having two perpendicular directions in which the in-plane Young's modulus is greater than 6 GPa, and having a moisture absorptivity of no greater than 3.3 wt% at 72% RH, 25° C.

2. A polyimide film according to claim 1, characterized in that X in structural unit (II) is represented by formula (II-i), with 40-70 mole percent of structural unit (I) and 30-60 mole percent of structural unit (II).

3. A polyimide film according to claim 1, characterized in that X in structural unit (II) consists of at least one group selected from among groups of formulas (II-ii), (II-iii) and (II-iv), with 70-95 mole percent of structural unit (I) and 10-40 mole percent of structural unit (II).

4. A polyimide film according to claim 1, characterized in that the imide group concentration, [imide] of the polyimide used is 5.7-6.2 eq/kg.

5. A polyimide film according to claim 2, characterized in that structural unit (II) is a structure represented by the following formula (II-a):



(II-a)

6. A polyimide film according to claim 1, characterized in that the tensile strength in one direction is 150 MPa or greater.

7. A polyimide film according to claim 1, wherein the imide group fraction of the polyimide is 95% or greater.

8. A film-forming process of a polyimide film characterized by comprising the following steps: